Statistical Thermodynamics in Chemistry and Biology

20. Coulomb's law of electrostatic forces

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Interactions between charges

This chapter:

- Electrostatic interactions govern many properties in physics, chemistry and biology.
- Salt concentrations regulate many processes in biology: transport through membranes; nerve systems are regulated by ion flux
- Technical applications in electrochemistry: batteries, corrosion, etc.
- Electrostatic interactions are long-range.
- Definition of the electric field.

- The interaction between two charges, q_1 and q_2, are given by an empirical law, Coulomb's law,

$$V(r) = \frac{q_1 q_2}{4\pi\varepsilon_0 r}$$

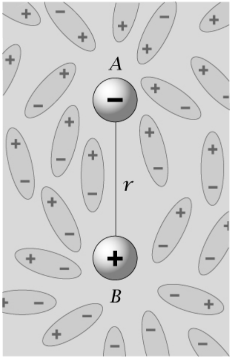
where ε_0 is the permittivity of vacuum.

Ionic interactions are weaker in a medium

- Ionic interactions are weakened in a medium, since the liquid is polarized.
- Basically three effects:
  - The electrons are polarized (increasing the dipole moment), described by the electronic polarizability.
  - The atoms within the molecule are moved further apart, described by the vibrational polarizability.
  - The molecular dipole moments are reoriented.
- Described by the dielectric constant, D (also called the *relative permittivity* ε_r),

$$V(r) = \frac{q_1 q_2}{4\pi\varepsilon_0 D r}$$

- Typical values: $D \approx 1$ (air); $D \approx 2$ (hydrocarbons, proteins); $D \approx 78$ (water)



Ionic interactions are strong and long-range

- Macroscopically, charge neutrality is a very strong condition.
- r^{-1} is the most long-range interactions.
- Nearest-neighbour interactions in a lattice (Bragg-Williams model) are not sufficient.
- Illustrated by the Bjerrum length, l_B, i.e. the distance where the elecrostatic energy equals the thermal energy RT,

$$RT = \frac{q_1 q_2}{4\pi\varepsilon_0 D l_B} \Rightarrow l_B = \frac{q_1 q_2}{4\pi\varepsilon_0 DRT}$$

- Typical values at room temperature: $l_B = 56$ nm (in air); scales with $\frac{1}{D}$: $l_B = 0.7$ nm (in water).

Electrostatic forces are pair-wise additive

- The force, $\vec{f}$ is given from the gradient of the energy,

$$\vec{f} = -\vec{\nabla}\frac{q_1 q_2}{4\pi\varepsilon_0 Dr} = \frac{q_1 q_2 \vec{r}}{4\pi\varepsilon_0 Dr^3}$$

- The Coulomb's law is pair-wise additive,

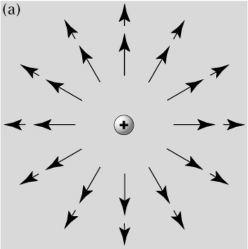
$$V(r) = \frac{1}{2}\sum_I \sum_{J\neq I} \frac{q_I q_J}{4\pi\varepsilon_0 Dr_{IJ}}$$

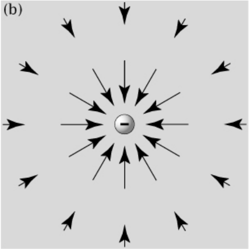
  so the force on a charge q_I is the sum of the force from all other charges q_J

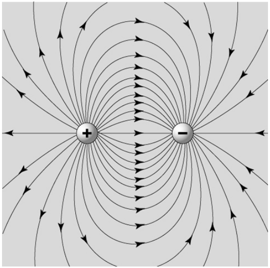
- The force on a test charge of unity size, $q_{\text{test}} = 1$, is defined as the electrostatic field,

$$\vec{E}\left(\vec{r}\right) = \frac{q\vec{r}}{4\pi\varepsilon_0 Dr^3}$$

Electric fields







Fluxes and electric fields

Gauss's law

- The electric field flux, Φ, through a surface is defined as

$$\Phi = \int_{\text{surface}} D\vec{E} \cdot d\vec{s}$$

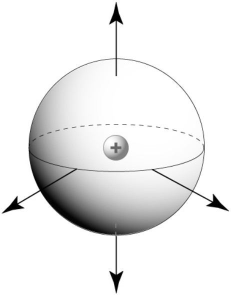
- Special case of a sphere:
  - The electric field in sperical polar coordinates (and no angular dependence),

$$E(r) = \frac{q}{4\pi\varepsilon_0 D r^2}$$

  - The area is $4\pi r^2$.
  - The flux,

$$\Phi = DE(r) \int_{\text{surface}} ds = DE(r) 4\pi r^2 = \frac{q}{\varepsilon_0}$$

  - A simple and useful expression (independent of the radius of the sphere).



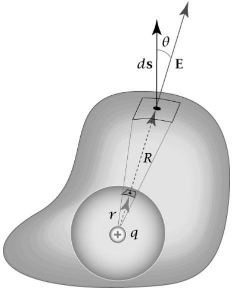
Generalization of electric field flux

- Skipping the derivation...
- For any shape of the surface and for many charges,

$$\Phi = \int_{\text{surface}} D\vec{E} \cdot d\vec{s} = \frac{1}{\varepsilon_0} \sum_{i=1}^{n} q_i$$

  which is called Gauss's law.
- Instead of a set of point charges, we may have a charge distribution, $\rho(r)$,

$$\Phi = \int_{\text{surface}} D\vec{E} \cdot d\vec{s} = \frac{1}{\varepsilon_0} \int_V \rho dV$$



Summary

- Coulomb's law
- Electric fields
- Gauss's law